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RILEM TC 281-CCC Working Group 6: Carbonation of Alkali Activated Concrete—Preliminary Results of a Literature Survey and Data Analysis

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Abstract. The current understanding of the carbonation of alkali-activated concretes is hampered *inter alia* by the wide range of binder chemistries used. To overcome some of the limitations of individual studies and to identify general correlations between their mix design parameters and carbonation resistance, the RILEM TC 281-CCC working group 6 compiled carbonation data for alkali-activated concretes and mortars from the literature. For comparison purposes, data for blended Portland cement-based concretes with a high percentage of SCMs ($\geq$ 66% of the binder) were also included in the database. A preliminary analysis of the database indicates that *w*/CaO ratio and *w*/b ratio exert an influence on the carbonation resistance of alkali-activated concretes but, contrary to what has been reported for concretes based on (blended) Portland cements, these are not good indicators of their carbonation resistance when considered individually. A better

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indicator of the carbonation resistance of alkali-activated concretes under conditions approximating natural carbonation appears to be their $w/(CaO + Na_2O + K_2O)$ ratio. Furthermore, the analysis points to significant shortcomings of tests at elevated CO_2 concentrations for low-Ca alkali-activated concretes, indicating that even at a concentration of 1% CO_2, the outcomes may lead to inaccurate predictions of the carbonation coefficient under natural exposure conditions.

Keywords: Alkali-activated materials · Carbonation · Natural exposure · Accelerated testing

1 Introduction

The carbonation of cementitious materials is an important degradation phenomenon, in many cases being the limiting factor for the service life of reinforced concrete structures. For concretes based on conventional cements (Portland and blended Portland cements), the w/CaO_{reactive} ratio has been found to be the major parameter determining their carbonation resistance [1, 2]; related to this ratio are concepts that involve w/b ratio and clinker content [3] as well as the k-value concept of EN 206 [4]. However, for concretes and mortars based on alkali-activated binders and other alternative cements these approaches seem to be not applicable without restrictions [5, 6]. Relatedly, the factors and mechanisms determining the carbonation resistance of alkali-activated concretes are not yet fully understood, partly due to the wide range of binder chemistries and the fact that individual carbonation studies are generally limited to only a few mix designs, curing conditions and exposure conditions [7].

To contribute to these issues, the RILEM TC 281-CCC working group 6 compiled carbonation data for a wide range of alkali-activated concretes and mortars from the literature. This has been done with the aim of resolving the shortcomings of individual studies and to identify general correlations between mix design parameters of alkali-activated concretes and their carbonation resistance. For comparison purposes, data for blended Portland cement-based concretes with a high percentage of supplementary cementitious materials (SCMs) in the binder were included in the database. In this paper, the database, the assumptions made in the evaluation of the data, and preliminary results and conclusions are presented.

2 Survey Scope and Data Processing

2.1 Data Inventory

The scientific literature was searched for studies that report carbonation depth (d_c)-*versus*-carbonation duration (t) data for alkali-activated concretes or mortars, or for concretes or mortars based on CEM III/B (according to EN 197−1; ≥ 66% blast furnace slag in the cement) or blended cements with at least 70% of other or mixed SCMs in the binder. Only data obtained at controlled relative humidity (conditions approximating indoor or "sheltered" natural carbonation and accelerated carbonation) were included in the database, while results for unsheltered natural exposure were not considered, as the degree of saturation of the pore systems of the exposed concretes is not controlled in the latter experiments. Carbonation data of pastes were not considered, as the potential effects of aggregates on the carbonation coefficient would not be observed. Studies with incomplete or internally inconsistent information about the mix design or the test conditions were also excluded from the database.

The mix designs of the concretes or mortars, the chemical compositions of the binders (solid precursors and activators), the physical properties of the constituents as well as curing, preconditioning and carbonation conditions were included in the database together with the respective carbonation depth data. In most of the studies, the carbonation depths were determined by spraying a phenolphthalein solution (usually 1%) on fracture surfaces; in one case alizarin yellow R was used as indicator, and in another case thin sections were examined.

The current database contains data for 74 concretes/mortars based on blended cements, *i.e.* binders with no activator other than Portland clinker (BCC); 125 concretes/mortars based on alkali-activated ground granulated blast furnace slag (GGBS-based AAC); 12 concretes/mortars based on alkali-activated fly ash or metakaolin (FA- or MK-based AAC); and 18 concretes/mortars based on other alkali-activated binders (other AAC). GGBS-based AAC are defined here as concretes/mortars with $\geq$ 50% GGBS in the solid fraction of the binder, *i.e.* excluding Na_2O, SiO_2 etc. dissolved in the liquid activator. FA- or MK-based AAC are defined as concretes/mortars with >50% fly ash or metakaolin, respectively, in the solid fraction of the binder; only one of the twelve materials was solely metakaolin-based. The other AAC include materials with binders based on municipal solid waste incineration bottom ash, silico-manganese slag or natural pozzolans; two hybrid cements were assigned to this class as well.

Most of the AAC were activated with sodium silicate solutions (of various SiO_2/Na_2O ratios), while fewer were activated with NaOH, Na_2CO_3, or a mixture of sodium silicate and Na_2CO_3. In some cases, portlandite [$Ca(OH)_2$] or gypsum [$CaSO_4 \cdot 2H_2O$] was employed as an additional activator,

2.2 Data Evaluation

When only one d_c-*versus*-t value was given for a specific material and carbonation conditions, the carbonation coefficient was calculated as $k = d_c/\sqrt{t}$, *i.e.* $d_c = 0$ mm at $t = 0$ d was implicitly assumed. When multiple d_c-*versus*-t values were available, the carbonation coefficient was obtained by first fitting a linear function to all available data points plotted as $d_c(\sqrt{t})$ up to $t = 1$ year. If that fit yielded a positive intercept with the ordinate, the slope of the function was used as k for the evaluation. If the fit yielded a negative intercept with the ordinate (*i.e.* a negative carbonation depth at $t = 0$ d, which would be unphysical), the fit was repeated with the linear function forced through the origin of the coordinates, and the value thus obtained was used. It is noted that the assumption of $d_c = 0$ mm at $t = 0$ d is not necessarily true, particularly for materials based on blended cements or alkali-activated binders [8, 9]. However, in the absence of data for the start of the exposure to CO_2, this assumption was made.

The data of the round robin testing programme of RILEM TC 247-DTA [8] was treated as if it was obtained in a single laboratory, using the average of the carbonation depths obtained in the participating institutes. However, the d_c obtained in lab G in that testing programme were not included in the present analysis, because that laboratory had employed a curing regime that differed from the curing in the other laboratories. The coefficient of variation (COV) of the d_c in the reduced dataset was in the range 21.2–42.1% for carbonation under conditions approximating natural exposure, and 1.0–45.4% for accelerated carbonation. To translate these uncertainties into the uncertainty of the resulting k, it was assumed that the COV of the latter was 40%, *i.e.* the standard deviation of the carbonation coefficient was estimated to be $0.40 \times k$.

In the following, k_{nat} will be used as the symbol for carbonation coefficients obtained under conditions approximating natural carbonation (sheltered), and k_{acc} will be used as the symbol for carbonation coefficients obtained under accelerated conditions. If the coefficients refer to a specified CO_2 concentration or concentrations, this will be noted in brackets (e.g., $k_{acc}[1\%]$).

From the mix designs of the concretes/mortars and the chemical compositions of their constituents, several parameters that may exert an influence on the carbonation resistance were computed. In cases where these parameters are water-to-oxide(s) mass ratios [*w*/oxide(s)], the value used for the oxide(s) is the total amount of that oxide(s) in the binder paste, including the contribution of the solid fraction of the activator. For example, w/Na_2O is the ratio between water and the total amount of Na_2O in the paste, *i.e.* the sum of the Na_2O contributed by the activator and the Na_2O present in the solid fraction of the binder. No attempt was made to discriminate "reactive" and "non-reactive" oxides in the paste, as this is usually not possible with high accuracy, if at all. The sum $Na_2O + K_2O$ is written as $(Na,K)_2O$ to reflect the fact that Na^+ and K^+ play a similar role in these binders and can be treated equivalently for the present purpose. However, all AAC in the current database were produced with Na-dominated activator solutions.

3 Preliminary Results and Discussion

3.1 Carbonation Under Conditions Approximating Natural Exposure

Figure 1 shows that the carbonation resistance of alkali-activated concretes and mortars cannot be predicted based on their *w*/CaO ratio alone. The FA-based AAC, and particularly the MK-based AAC, deviate considerably from a linear relationship that can be discerned for the combined BCC and GGBS-based AAC. Within the group of BCC, a good correlation between k_{nat} and *w*/CaO was observed, while a correlation was less evident in the GGBS-based AAC (Fig. 2). Compared to k_{nat} *versus* *w*/CaO, a slightly more reasonable correlation was obtained when plotting k_{nat} *versus* *w*/*b* of the GGBS-based AAC (Fig. 3B).

The observation that FA- and MK-based AAC do not follow the same trend as the BCC as regards *w*/CaO can be attributed to the fact that in binders with low CaO content, carbonation is determined to a large extent by the amount of alkali ions present in the pore solution [5, 10]. This is supported by a plot of k_{nat} *versus* $w/[CaO + (Na,K)_2O]$ (Fig. 4). In this plot, a correlation between the two parameters is evident for all concretes combined, though the scatter of the data is considerable. In particular, there is significant deviation between the MK-based and FA-based AAC with comparatively high k_{nat}, indicating that additional parameters substantially influence the carbonation resistance of these concretes.

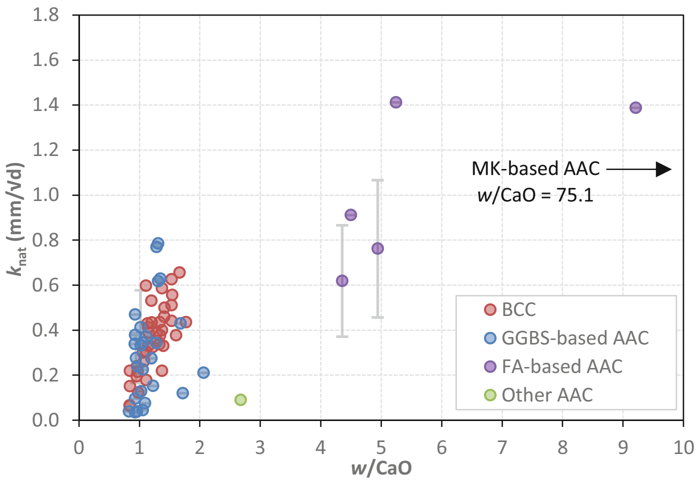

Fig. 1. Carbonation coefficients obtained under conditions approximating natural carbonation *versus w*/CaO ratio. Error bars represent the estimated standard deviations of the results obtained by RILEM TC 247-DTA.

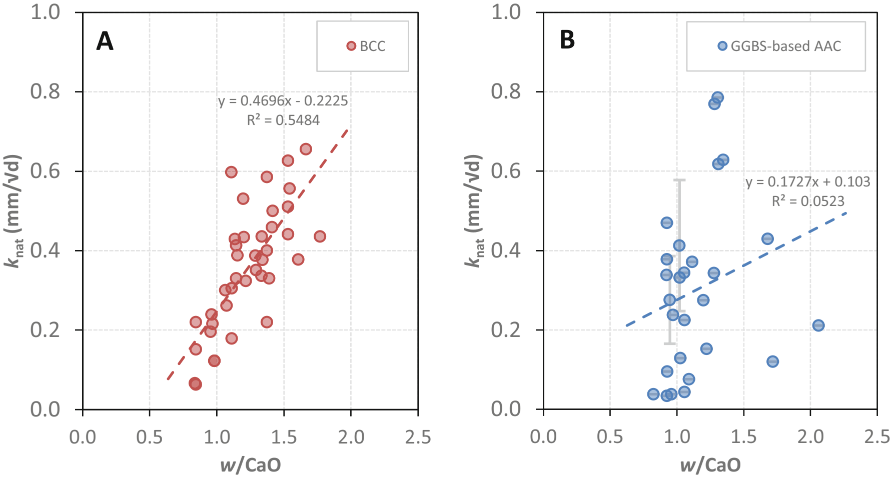

Fig. 2. Carbonation coefficients obtained under conditions approximating natural carbonation *versus w*/CaO ratio (**A**, BCC; **B**, GGBS-based AAC). Error bars represent the estimated standard deviations of the results obtained by RILEM TC 247-DTA.

3.2 Accelerated Carbonation

Accelerated carbonation testing involves exposing concrete or mortar samples to CO_2 concentrations (c_{CO2}) higher than the natural CO_2 concentration present in air (~0.04% CO_2). Assuming that the square root-of-time law holds for estimating the depth of carbonation, the relationship between the carbonation coefficients obtained with accelerated

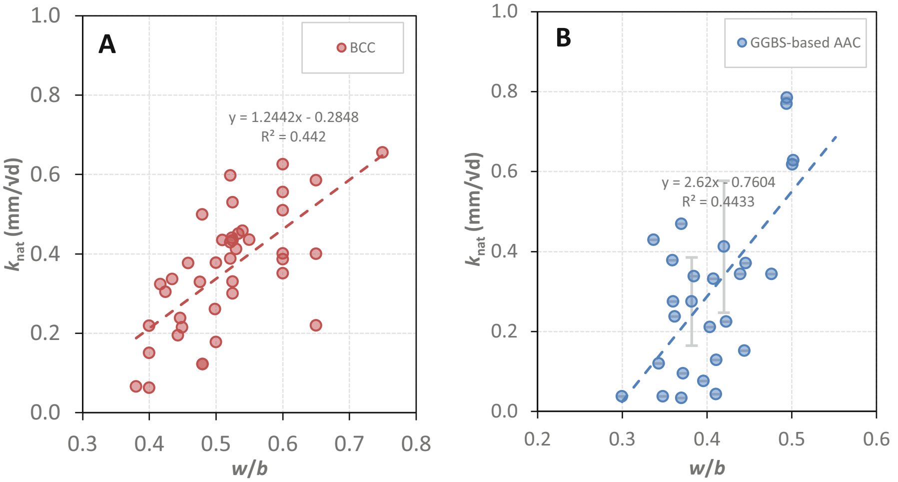

Fig. 3. Carbonation coefficients obtained under conditions approximating natural carbonation *versus w*/*b* ratio (**A**, BCC; **B**, GGBS-based AAC). Error bars represent the estimated standard deviations of the results obtained by RILEM TC 247-DTA.

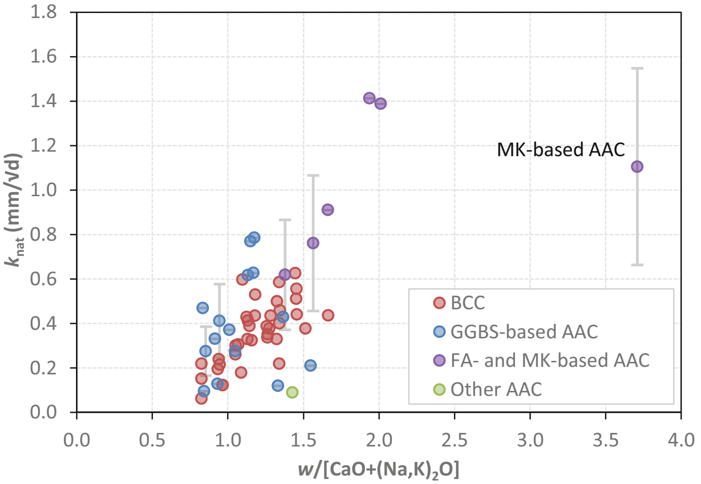

Fig. 4. Carbonation coefficients obtained under conditions approximating natural carbonation *versus w*/[CaO + (Na,K)$_2$O] ratio. Error bars represent the estimated standard deviations of the results obtained by RILEM TC 247-DTA.

carbonation and natural carbonation can be derived as [11, 12]:

$$k_{\mathrm{acc}}/k_{\mathrm{nat}} = \sqrt{(c_{\mathrm{CO2,acc}}/c_{\mathrm{CO2,nat}})} \tag{1}$$

For example, inserting 1% for $c_{CO2,acc}$ and 0.04% for $c_{CO2,nat}$ yields $k_{acc}[1\%]/k_{nat} = \sqrt{(1/0.04)} = 5$. There are some experimental data supporting at least the approximate validity of Eq. (1) for BCC [6, 12], though the deviations between computed and measured carbonation coefficients can be significant [1, 4].

Figure 5 shows that for BCC and GGBS-based AAC the relationship between k_{acc} and k_{nat} appears to generally conform to Eq. (1), while FA- and MK-based AAC yield considerably lower k_{acc} than what would be expected from Eq. (1). The finding that the behaviour of the FA- and MK-based AAC deviates significantly from the expected relationship between k_{acc} and k_{nat} has important implications. Notably, it indicates that the outcomes of accelerated carbonation testing of low-Ca alkali-activated materials (even at $c_{CO2} = 1\%$) lead to inaccurate predictions of their carbonation resistance under natural exposure. However, the number of available studies of these materials that include accelerated and natural carbonation testing results for the same materials is currently very limited; thus, additional data is required to verify the above conclusion. It is also noted that the testing programme of RILEM TC 247-DTA [8] gave similar ranking of a diverse set of AAC in natural and accelerated carbonation testing, indicating the usefulness of accelerated testing at least for this purpose.

The present analysis further indicates that even for GGBS-based AAC (*i.e.* high-Ca alkali-activated materials) and—in line with a previous analysis of RILEM TC 281-CCC [4]—for BCC the informative value of accelerated carbonation testing is limited. For example, no relationship between k_{acc} and w/CaO is apparent for CO_2 concentrations of 1% and 3–5% (Fig. 6). When k_{acc} is compared with $w/[CaO + (Na,K)_2O]$ (Fig. 7), a correlation may possibly exist for $c_{CO2} = 1\%$ for the BCC, the GGBS—and the FA-based AAC, but for $c_{CO2} = 3–5\%$ no relationship can be discerned. Consideration of the MgO content of the binders did not lead to a significant improvement, *i.e.* did not enable the observation of any clear relationship. It is also possible that this relates to deviations from the assumptions that underpin the use of the square root-of-time relationship to obtain a characteristic coefficient to describe carbonation kinetics for materials that differ significantly from plain Portland cement; this merits further investigation.

4 Concluding Remarks

The reported data for carbonation resistance of alkali-activated concretes and mortars are very unevenly distributed: While a comparatively high number of studies concerning GGBS-based AAC could be found, only a small number of studies measuring the carbonation performance of FA– and MK-based AAC appear to exist. Slightly more data concerning "other" AAC, *i.e.* materials with binders based on municipal solid waste incineration bottom ash, non-ferrous slag or natural pozzolans, are available, but the majority of these were obtained under highly accelerated carbonation conditions, e.g. with $c_{CO2} \geq 10\%$; thus, these results might not be directly comparable with those obtained under lower CO_2 concentrations.

An equally important issue is the comparison of results of accelerated carbonation conditions with results of conditions approximating natural exposure: While several studies have investigated this issue for Portland cement concretes and BCC, there is only limited data available in this regard for GGBS-based AAC, and only two major studies [8, 13] were found for FA–and MK-based AAC.

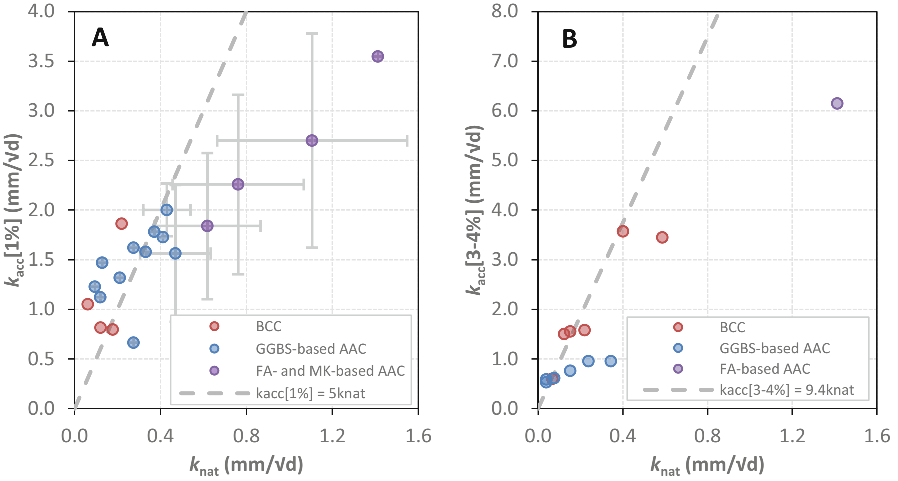

Fig. 5. Carbonation coefficients obtained under accelerated conditions (**A**, $c_{CO2} = 1\%$; **B**, $c_{CO2} = 3–4\%$) *versus* the carbonation coefficients obtained under conditions approximating natural exposure. Error bars represent the estimated standard deviations of the results obtained by RILEM TC 247-DTA.

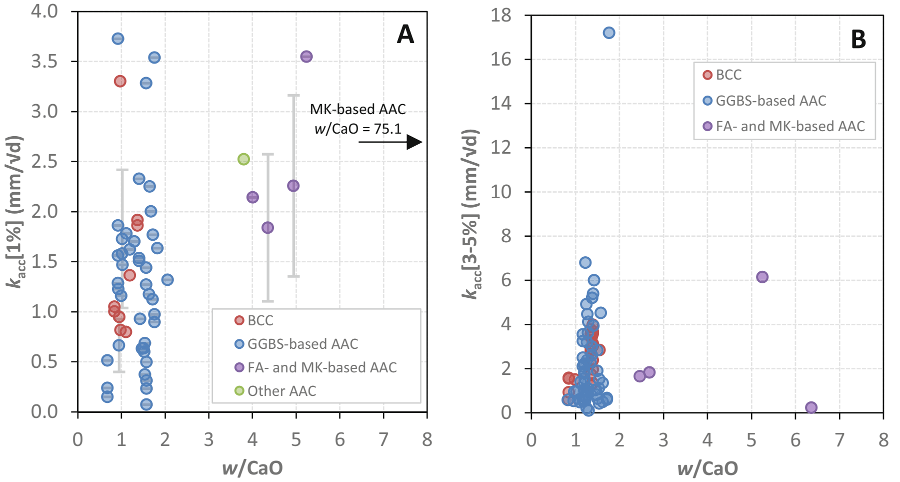

Fig. 6. Carbonation coefficients obtained under accelerated conditions (**A**, $c_{CO2} = 1\%$; **B**, $c_{CO2} = 3–5\%$) *versus* *w*/CaO ratio. Error bars represent the estimated standard deviations of the results obtained by RILEM TC 247-DTA.

Thus, to better understand the carbonation of alkali-activated materials as a class of cements, *i.e.* over their complete range of chemistries, and to reliably apply accelerated carbonation testing methods to these materials, it will be necessary to obtain more data on the carbonation resistance of low-Ca alkali-activated concretes and mortars with a focus on the comparison between accelerated conditions and conditions approximating natural

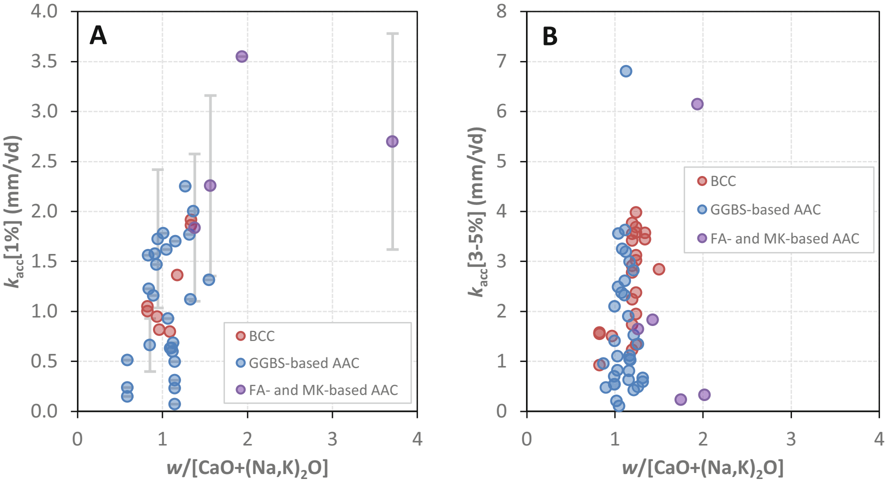

Fig. 7. Carbonation coefficients obtained under accelerated conditions (**A**, $c_{CO2} = 1\%$; **B**, $c_{CO2} = 3–5\%$) *versus* w/[CaO + (Na,K)$_2$O] ratio. Error bars represent the estimated standard deviations of the results obtained by RILEM TC 247-DTA.

exposure. Though not touched by the present analysis, it appears also necessary to focus on the effects of different relative humidities in the laboratory and under unsheltered natural conditions (*cf*. Ref. [1]).

As regards the present analysis, with the limitations as described, two findings are particularly significant:

(1) The carbonation coefficient under conditions approximating natural exposure appears to be related to the binder w/[CaO + (Na,K)$_2$O] ratio, but not the w/CaO ratio, for GGBS- and FA-based AAC. However, the scatter of the data is considerable; thus, the former ratio may serve at best as a rough indicator of the carbonation resistance.

(2) For FA- and MK-based AAC (low-Ca alkali-activated materials), accelerated carbonation testing leads to considerably lower carbonation coefficients than what would be expected from the square root-of-time law; thus, the application of that law to predict the carbonation resistance of these concretes under natural conditions may be inaccurate. Due to the limitations of the present database, however, additional work is required to verify this conclusion.

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